Co, Cu, Ni, AND Ca SORPTION BY A MIXED SUSPENSION OF SMECTITE AND HYDROUS MANGANESE DIOXIDE

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Abstract—The sorption properties of Co, Cu, Ni, and Ca were studied in a mixed mineral suspension of synthetic MnO_2 and Wyoming montmorillonite. The distribution of the sorbed cations between the two solid phases was measured by indirect chemical fractionation with acidified $NH_2OH\text{-}HCl$ and by direct X-ray spectroscopic analysis of mineral particles using electron microscopy. Electron microscope and $NH_2OH\text{-}HCl$ measurements of the quantity of Co sorbed on MnO_2 agreed within 6%. Seventy-seven, 67, and 69% of the total Co, Cu, and Ni sorbed by the mixed mineral suspension was found on the manganese oxide. The opposite distribution was found for sorbed Ca with 28% on the manganese oxide and 72% on the montmorillonite particles. The observed differences in metal sorption by these minerals are related to the cation-sorption mechanisms of manganese oxide and montmorillonite.

Key Words—Adsorption, Analytical transmission electron microscopy, Birnessite, Cation exchange, Manganese oxide, Montmorillonite, Transition metals.

INTRODUCTION

The solubility of many transition metal ions in soils and sediments is thought to be controlled by sorption on hydrous manganese oxides (McKenzie, 1967; McLaren and Crawford, 1973a, 1973b; McLaren *et al.,* 1981). These reactions occur in the presence of other minerals, thus manganese oxides must be able to compete with other mineral phases for transition metal sorption. Indirect evidence for such competition has been provided by selective chemical dissolution of transition metal amended soils and by statistical comparison of metal sorption by whole soils and sediments to that by model soil minerals and organic separates (McKenzie, 1967; McLaren and Crawford, 1973a, 1973b; McLaren *et al.,* 1981). Whereas these studies provide some indication of the quantity of metal ions sorbed by the manganese oxides, they do not present direct evidence of competitive sorption reactions between manganese oxides and other soil minerals; thus, such reactions remain in the realm of conjecture. Direct evidence can only be obtained through the use of an analytical procedure which enables a chemical analysis of a mineral surface to be made. This condition is met in transmission electron microscope (TEM) X-ray spectrometry. Although this analytical technique has been used by several workers to study metal distributions in individual minerals there has been little application of it to the study of metal sorption by mixed mineral systems.

In this paper, the results of a TEM study of metal ion sorption by a mixed system of synthetic manganese oxide and Wyoming montmorillonite are presented. This study was conducted to evaluate the applicability of the TEM analysis to mixed-mineral sorption experiments and to provide direct, conclusive evidence of metal ion sorption by manganese oxides in the presence of a competing sorbent mineral. A spectroscopic analysis of individual particles showed that Co, Cu, and Ni sorption in this assemblage occurred mainly on MnO_2. Ca sorption was more evenly distributed between the two minerals.

MATERIALS AND METHODS

Mineral preparation

The manganese oxide used in this study was a synthetic birnessite prepared after McKenzie (1971) by the addition of HCl to hot $KMnO_4$. Details of the oxide synthesis and characterization are presented elsewhere (Traina and Doner, 1985).

Montmorillonite from Crook County, Wyoming (sample SWy-1 from the Source Clay Minerals Repository of The Clay Minerals Society) was saturated with Na^+ and rinsed with 0.01 M NaCl to reduce the ionic strength to 0.01. The $<0.5\text{-}\mu m$ fraction was removed by centrifugation, diluted with 0.01 M NaCl to a suspension density of 0.01919 g clay/g of suspension, and saved for the metal sorption experiments.

Metal sorption

A stock manganese oxide suspension was prepared by dispersing 1.00 g of oxide in 200 ml of 0.02 M NaCl in a 250-ml polycarbonate bottle. The resulting mixture was allowed to hydrate for 24 hr prior to use.

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Mixed mineral suspensions of clay and oxide were prepared by adding 1 ml of the birnessite suspension and 1 ml of the montmorillonite suspension to 37 ml of pH 3.88, 0.02 M NaCl in 50-ml polycarbonate centrifuge tubes. The metal sorption capacities for birnessite was determined in preliminary experiments with pure oxide suspensions at pH 4 in 0.02 M NaCl to be 3.72, 3.64, 2.22, and 1.95 meq/g for Co, Cu, Ni, and Ca sorption, respectively. The metal-sorption capacity for the montmorillonite was taken to be equal to its cation-exchange capacity of 0.92 meq/g (Sposito *et al.,* 1981). The ratio of oxide to smectite used for all sorption experiments in this study was based on the maximum Co-sorption capacity of birnessite. Thus, in the mixed mineral suspension the Co-sorption capacity of birnessite was equal to that of montmorillonite.

The suspension pH was 4.2 prior to metal ion addition. This low pH was chosen to minimize potential experimental complications resulting from the formation of metal-hydroxide species. Appropriate amounts of metal chlorides were added to give initial concentrations of 0 to 383 μM Co, 345 μM Ni, 390 μM Cu, and 113 and 300 μM Ca. The suspension was diluted to 40 ml with pH 3.88, 0.02 M NaCl, and the centrifuge tubes were capped and shaken at 25°C. The samples were shaken for 7 days to conform to the experimental conditions of a previous study (Traina and Doner, 1985), after which the suspension pH was measured. The samples were centrifuged at 12,060 RCF, the supernatant was decanted and filtered with Nucleopore, 0.2-μm membrane, and the filtrate was analyzed directly for the appropriate metal ions with flame atomic absorption spectrophotometry (AAS). The clay-oxide pads were redispersed and washed in H_2O until Cl^- ions could not be detected in the supernatant with $AgNO_3$. Ten microliters of this suspension was placed onto Formvar-coated, gold support grids, allowed to air dry, and coated with carbon for stabilization. The remainder of the oxide-smectite mixture from the Co treatment was shaken for 30 min with acidified NH_2OH-HCl after Chao (1972) to dissolve the birnessite selectively. The resulting solutions were analyzed directly for the appropriate metal ions by AAS.

Spectroscopic analysis of the mineral samples was made with a Jeol JEM-100 C-type transmission electron microscope. The X-ray detection system consisted of a United Technology-Microtrace, Li-drifted Si-detector and a Tracor Northern multichannel analyzer. The microscope was operated at an accelerating voltage of 100 kV. The differences in particle morphology and electron diffraction patterns allowed for easy distinction of the two minerals. Isolated, individual particles were chosen for analysis to eliminate detection of X-rays generated by adjacent particles. X-ray analysis was accomplished by condensing the electron beam onto an individual particle and adjusting the beam shape with the stigmator controls to conform to the shape of par-

ticle. X-ray intensities for each particle were counted for a period of 2 min, and the integrated peak heights for each element were recorded. Counts were taken for 12 oxide particles and 12 smectite particles for each metal treatment. The total metal sorbed was calculated from the difference in initial and final metal concentrations. The partitioning of a sorbed metal between birnessite and montmorillonite was based on the relationship:

$$I_{Me}/I_{Mn} = k(C_{Me}/C_{Mn}),$$

where k is a proportionality factor determined from Co-, Cu-, and Ni-treated birnessites of known composition and standard phyllosilicate mineral samples kept in the Department of Geology and Geophysics, University of California, Berkeley, California; I_{Mn} is the measured average X-ray intensities of Mn in the oxide particles; C_{Mn} is the weight fraction of Mn in the oxide structure (0.63). I_{Me} and C_{Me} are the average of the measured X-ray intensities and the calculated weight fraction of the sorbed ion, respectively. The concentration of sorbed metal ions on the smectite was taken as the difference between the total amount sorbed by the entire mixed suspension and the amount present on the oxide as determined by TEM.

RESULTS

The sorption of Co, Cu, and Ni resulted in a decrease in suspension pH to 3.68 for the highest level of Co sorption, and 3.61 and 3.93 for Cu and Ni sorption, respectively. A change in pH was not observed during Ca sorption. Co, Cu, Ni, and Ca sorption all resulted in visible flocculation of the smectite particles.

Average intensity ratios and coefficients of variation for each metal treatment are given in Table 1. An increase in the initial concentrations of sorbate ions resulted in an increase in I_{Me} for the birnessite particles and an increase in the precision of the X-ray counting. The sorbate concentrations on the smectite particles were too low to allow accurate counting of energy dispersive X-rays, so the level of metal sorption by these particles was calculated from the difference in the metal sorbed by the entire suspension as determined by AAS and the amount of metal sorbed by the birnessite as determined by TEM.

Figure 1 compares the TEM determination of Co sorption by birnessite (in the mixed mineral suspension) with the NH_2OH-HCl selective dissolution technique. The linear relationship between the two kinds of analysis suggested that the TEM technique could be used with confidence to partition metal sorption in this system. Cobalt sorption by the mixed suspension was dominated by metal sorption on birnessite. Figure 2 shows the solid phase distribution of the sorbed Co as determined by TEM. This metal was strongly partitioned onto the oxide. At low levels of metal application, Co was sorbed entirely by birnessite particles.

Table 1. X-ray intensity ratios for Co-, Cu-, Ni-, and Ca-sorbed birnessite.

Me	Initial concentration (μmole/liter)	I_{Me}/I_{Mn}[1]	Standard deviation (μmole/liter)
Co	24	0.029	0.003
Co	49	0.061	0.006
Co	94	0.114	0.010
Co	155	0.155	0.013
Co	201	0.160	0.010
Co	256	0.180	0.010
Co	383	0.200	0.011
Cu	390	0.300	0.020
Ni	345	0.140	0.029
Ca	113	0.020	0.005
Ca	300	0.023	0.010

[1] Values reported for I_{Me}/I_{Mn} are the means of 12 measurements.

Figure 1. Quantity of Co sorbed by birnessite in the mixed mineral suspension as determined by transmission electron microscopy analysis and NH_2OH-HCl.

Cobalt sorption by the montmorillonite was only observed when the initial sorbate concentration was equal to or greater than 155 μM. This value corresponded to an equilibrium Co concentration of 13.5 μM. At the highest level of Co application, 77% of the Co sorbed by the mixed suspension was on the oxide. At this level Co satisfied roughly 100% and 17% of the sorption capacities of the oxide and smectite, respectively. It should be noted that a small release of Mn to solution was observed during Co sorption, but this accounted for less than 0.1% of the Mn present in the oxide structure and thus was insignificant in calculating the amount of Co sorbed by the birnessite particles.

Cu and Ni were strongly partitioned onto the birnessite particles. The levels of metal sorption (1.82 and 1.11 mole/kg) corresponded to 100% of sorption capacity of birnessite and roughly 30 and 17% (0.16 and 0.09 mole/kg) of the sorption capacity of montmorillonite for the respective metal ions.

Ca was not as strongly sorbed by the mixed suspension as were the heavy metals (0.47 and 0.22 mole/kg for birnessite and montmorillonite, respectively). Although Ca was still partitioned onto the oxide particles, it filled a smaller portion of the oxide's sorption capacity. At an equilibrium concentration of 150 μM, 48% of the Ca sorption capacity of birnessite and 48% of the exchange capacity of the montmorillonite were satisfied by Ca ions.

DISCUSSION

The strong agreement between the TEM and the NH_2OH-HCl measurements of Co sorption by birnessite (Figure 1) indicates that both of these techniques could be used to measure metal-ion sorption by manganese oxides in mixed mineral systems. A distinct advantage, however, is obtained by usi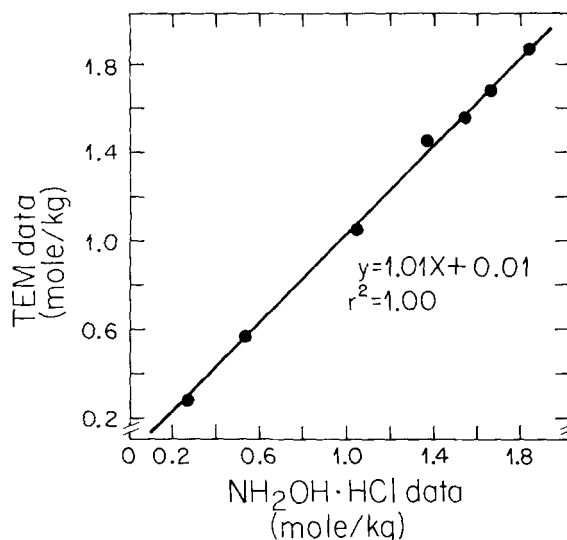ng the TEM method. Unlike chemical extraction procedures, energy dispersive X-ray analysis is a direct measurement and thus can provide a definite assessment of sorbed-metal distributions. The main constraint in the TEM technique is the need for relatively high sorbate surface concentrations to allow accurate X-ray detection. Although this condition was met for the oxide particles in this study, it was not achieved for the smectite particles. Therefore, although the partitioning of metals onto the oxide particles was determined by direct measurement, the metal concentration on the smectite particles was based on a difference calculation.

It should be noted that the total dissolution of the birnessite by the NH_2OH-HCl treatment generated large amounts of solution Mn^{2+}. The presence of Mn^{2+} in solution should have resulted in some exchange of the
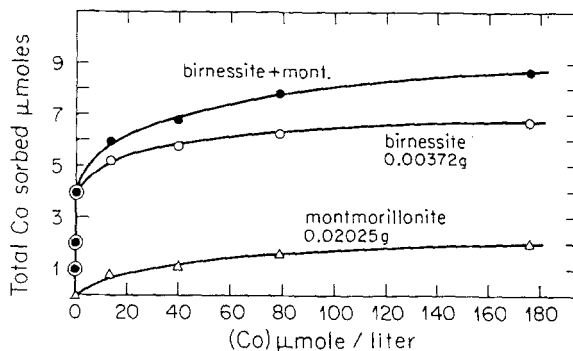

Figure 2. Total Co sorbed by the entire mixed suspension and by each mineral phase as determined by transmission electron microscopy.

sorbed metal ions from the smectite, but the close agreement between the TEM and NH_2OH-HCl measurements of Co sorption suggested that exchange did not occur. It is possible that the 30-min reaction time used in the chemical dissolution procedure was not long enough to allow for the Mn^{2+} to diffuse into the flocculated smectite particles and to exchange for the sorbed metal ions.

The saturation of the oxide surfaces by Co, Cu, and Ni indicates that the sorption of these metals by birnessite was not inhibited by competition with montmorillonite. Inasmuch as the ratio of birnessite to montmorillonite provided equal sorption capacities for the two minerals, the differential partitioning of cations between the clay and oxide particles can not be attributed to differences in the sorption capacities of each mineral, but must have resulted from different metal ion-mineral bonding energies. These results suggest that heavy metal sorption by MnO_2 involves a strong coordination of the sorbate with the oxide surface. Such coordination is consistent with Murray's (1975) suggestion that divalent cation sorption of MnO_2 involves an exchange for surface bound protons as shown below:

$$\underline{MnOH}^\circ + Me^{2+} = \underline{MnOMe}^+ + H^+,$$
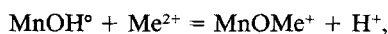
where the underlined species represent oxide surface sites. Where the sorbate is a heavy metal this reaction generally exhibits a molar metal-proton exchange stoichiometry of 1:1 (Murray, 1975; McKenzie, 1979; Traina and Doner, 1985). In addition, large amounts of heavy metals have been shown to sorb onto MnO_2 at the oxide's point of zero charge (pzc approximately equal to pH 2, Murray et al., 1968; Murray, 1974; McKenzie, 1981; Oscarson et al., 1983), implying that attractive forces other than coulombic interactions are responsible for sorption of these ions (Murray et al., 1968). In contrast, alkaline earth cations are minimally sorbed at the pzc and exhibit a molar proton-metal exchange stoichiometry of 0.3, suggesting that coulombic forces play a greater role in the sorption of these ions (Murray, 1975). Because Na sorption by MnO_2 does not occur at the oxide's pzc (Murray et al., 1968) and Na sorption at pH 4.0 releases little H^+ (Loganathan and Burau, 1973), the interaction of Na with birnessite is thought to be controlled almost entirely by coulombic forces.

Cation sorption by expanding aluminosilicates is considered to be primarily due to coulombic attraction of the metal ions by permanent, negative charges on the mineral structure. For this reason, cation sorption by montmorillonite should be strongly influenced by the concentrations of all cations present in solution.

The greater sorption of the metals by the birnessite particles was most likely due to the above-mentioned differences in the sorption mechanisms of clays and oxides. These differences resulted in differing degrees of competition between Na and the other metal ions

for the available sorption sites on each mineral. The presence of 0.02 M Na provided strong competition for heavy metal sorption by the montmorillonite but had little effect on the sorption of these ions by birnessite. Thus Co, Cu, and Ni were strongly attracted to the birnessite particles resulting in the marked fractionation of these metals onto the oxide. Because Ca interactions with birnessite and montmorillonite were largely controlled by coulombic forces, competition with Na mainly controlled Ca sorption by both minerals, resulting in a more even distribution of Ca between the two solid phases with Ca satisfying 48% of the sorption capacity of birnessite and montmorillonite.

Cation sorption by birnessite and smectite has been shown to increase with increased pH (Kinniburgh and Jackson, 1981). Further study is needed to evaluate the differential partitioning of sorbed transition metal ions between these minerals at pHs >4.0; however, high concentrations of transition metals are typically associated with manganese oxides in marine sediments (Burns and Burns, 1979). This association suggests that manganese oxides can compete with other minerals for the sorption of transition metals above pH 4.0.

CONCLUSIONS

These results indicate that energy dispersive X-ray analysis during electron microscopy can provide a direct measurement of the partitioning of sorbed cations onto specific mineral phases in mixed mineral systems. Inasmuch as a relatively high surface concentration of sorbate is needed for accurate X-ray detection, this analytical technique is most useful in the study of metal sorption to minerals with high surface charge densities, such as hydrous metal oxides.

In the mixed system of birnessite and montmorillonite, transition metals were sorbed mainly by the MnO_2, whereas sorbed Ca was more prevalent on the montmorillonite. These results provide direct, conclusive evidence that manganese oxides will sorb metal ions in the presence of competing sorbents. Metal partitioning in this system can not be described by consideration of the relative sorption capacities of each individual mineral. Instead, consideration must be given to the sorption affinities for each cation-mineral pair.

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Резюме—Изучались сорбционные свойства Co, Cu, Ni, и Ca в суспензиях смешанных минералов-синтетической MnO_2 и вайомингского монтмориллонита. Распределение сорбираванных катионов между двумя твердыми фазами измерялось при помощи химического фракционирования с подкисленным NH_2OH-HCl и при помощи прямого рентгеновского спектрального анализа частиц минералов, используя электронную микроскопию. Результаты измерений количества Co, сорбированного на MnO_2, при помощи электронного микроскопа и NH_2OH-HCl совпадали с точностью до 6%. Семьдесят семь, 67, и 69% общего количества Co, Cu, и Ni, сорбированных суспензией смешанных минералов, было обнаружено на двуокиси марганца. Противоположное распределение было обнаружено для сорбированного Ca—28% на двуокиси марганца и 72% на монтмориллонитовых частицах. Наблюдаемые разницы в сорбции металлов этими минералами связаны с механизмами сорбции катионов двуокисью марганца и монтмориллонитом. [E.G.]

Resümee—Es wurden die Sorptionseigenschaften von Co, Cu, Ni, und Ca in einer gemischten Mineralsuspension aus synthetischem MnO_2 und Montmorillonit von Wyoming untersucht. Die Verteilung der sorbierten Kationen zwischen den zwei festen Phasen wurde durch indirekte chemische Fraktionierung mit angesäuertem NH_2OH-HCl und durch direkte röntgenspektroskopische Analyse mittels Elektronenmikroskopie der Mineralteilchen gemessen. Elektronenmikroskopische und NH_2OH-HCl-Messungen der an MnO_2 adsorbierten Co-Menge stimmten innerhalb von 6% überein. Es zeigte sich, daß am Manganoxid 77, 67, bzw. 69% der gesamten durch die gemischte Mineralsuspension adsorbierten Co-, Cu-, und Ni-Menge adsorbiert wurde. Die umgekehrte Verteilung wurde für das sorbierte Ca gefunden, wobei 28% am Manganoxid und 72% an den Montmorillonitteilchen adsorbiert waren. Die beobachteten Unterschiede bei der Metallsorption durch diese Minerale hängen mit dem Kationensorptionsmechanismus von Manganoxid und Montmorillonit zusammen. [U.W.]

Résumé—Les propriétés de sorption de Co, Cu, Ni, et Ca ont été étudiées dans une suspension de minéraux mélangés consistant de MnO_2 synthétique et de montmorillonite du Wyoming. La distribution des cations sorbés entre les deux phases solides a été mesurée par fractionation chimique indirecte avec du NH_2OH-HCl acidifié et par l'analyse spectroscopique directe des rayons-X des particules minérales utilisant la microscopie électronique. Les mesures obtenues du microscope électronique et de NH_2OH-HCl de la quantité de Co sorbée sur MnO_2 étaient à 6% pres. Soixante dix-sept, 67, et 69% du Co, Cu, et Ni total sorbé par la suspension de minéraux melangés ont été trouvés sur l'oxide de manganèse. Une distribution opposée a été trouvée pour le Ca sorbé avec 28% sur l'oxide de manganèse et 72% sur les particules de montmorillonite. Les différences observées de sorption de métal de ces minéraux sont associées aux mécanismes de sorption de cations de l'oxide de manganèse et de montmorillonite. [D.J.]